

We Claim:

1. A method for purifying a mixture comprising single-wall carbon
nanotubes and amorphous carbon contaminate, said method comprising the steps
5 of:
 - (a) heating said mixture under oxidizing conditions sufficient to remove
the said amorphous carbon and
 - (b) recovering a product comprising at least about 80% by weight of
single-wall carbon nanotubes.
- 10 2. The method of claim 1 wherein said oxidizing conditions comprise
an aqueous solution of an inorganic oxidant.
3. The method of claim 2 wherein said inorganic oxidant is selected
from the group consisting of nitric acid, a mixture of sulfuric acid and hydrogen
peroxide, potassium permanganate and mixtures thereof.
- 15 4. The method of claim 2 wherein said aqueous solution is heated to
reflux.
5. The method of claim 2 additionally comprising the step of subjecting
the oxidized product of step (b) to a saponification treatment.
6. The method of claim 5 wherein said saponification treatment
20 comprises contacting said product with a basic solution.
7. The method of a claim 6 wherein said basic solution comprises
sodium hydroxide.
8. The method of claim 6 additionally comprising the step of
neutralizing the saponified product with an acid.
- 25 9. The method of claim 8 wherein said acid is hydrochloric acid.
10. The method of claim 8 additionally comprising the step of recovering
a solid product from the saponified, neutralized product.
11. The method of claim 10 wherein said product is recovered by a
method selected from the group consisting of filtration, settling by gravity, chemical
30 flocculators, and liquid cycloning.

12 The method of claim 10 wherein said solid product is a paper-like two dimensional product.

13. The method of claim 12 additionally comprising the step of drying the product.

5 14. The method of claim 13 wherein said product is dried at about 850°C in a hydrogen gas atmosphere.

15. The method of claim 1 wherein said product comprises at least about 90% by weight of single-wall carbon nanotubes.

10 16. The method of claim 1 wherein said product comprises at least about 95% by weight of single-wall carbon nanotubes.

17. The method of claim 1 wherein said product comprises at least about 99% by weight of single-wall carbon nanotubes.

18. A method for producing tubular carbon molecules of about 5 to 500 nm in length, said method comprising the steps of:

15 (a) cutting single-wall nanotube containing-material to form a mixture of tubular carbon molecules having lengths in the range of 5-500 nm;

(b) isolating from said mixture of tubular carbon molecules a fraction of said molecules having substantially equal lengths.

20 19. The method of claim 18 wherein said cutting single-wall nanotubes into tubular carbon molecules comprising the steps of:

(a) forming a substantially two-dimensional target containing single-wall nanotubes of lengths up to about one micron or more, and

(b) irradiating said target with a high energy beam of high mass ions.

25 20. The method of claim 19 wherein a high energy beam is produced in a cyclotron and has an energy of from about 0.1 to about 10 GeV.

21. The method of claim 19 wherein said high mass ion has a mass of greater than about 150 AMU.

30 22. The method of claim 21 wherein said high mass ion is selected from the group consisting of gold, bismuth and uranium.

23. The method of claim of 22 wherein the high mass ion is Au^{+33} .

24. The method of claim 18 wherein said cutting single-wall nanotubes into tubular carbon molecules comprises the steps of:

(a) forming a suspension of single-wall nanotubes in a medium;

5 (b) sonicating said suspension with acoustic energy.

25. The method of claim 24 wherein said acoustic energy is produced by a device operating at 40 KHz and having an output of 20 W.

26. The method of claim 18 wherein said cutting single-wall nanotubes into tubular carbon molecules comprises refluxing single wall nanotube material in
10 concentrated HNO_3 .

27. The method of claim 19 further comprising the step of heating the tubular carbon molecules to form a hemispheric fullerene cap on at least one end thereof.

28. The method of claim 18 further comprising the step of reacting said
15 tubular carbon molecules with a material which provides at the reaction conditions at least one substituent on at least one of said ends of said tubular carbon molecule.

29. The method of claim 26 further comprising the step of reacting said tubular carbon molecules with a material which provides at the reaction conditions at least one substituent on at least one of said ends of said tubular carbon molecule.

20 30. The method of claim 28 or 29 wherein said substituent is selected from the group consisting of each may be independently selected from the group consisting of hydrogen; alkyl, acyl, aryl, aralkyl, halogen; substituted or unsubstituted thiol; unsubstituted or substituted amino; hydroxy, and OR' wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl aralkyl,
25 unsubstituted or substituted amino; substituted or unsubstituted thiol; and halogen; and a linear or cyclic carbon chain optionally interrupted with one or more heteroatom, and optionally substituted with one or more $=\text{O}$, or $=\text{S}$, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2-8 amino acids.

30 31. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of:

- (a) providing at least about 10^6 tubular carbon molecules of substantially similar length in the range of 50 to 500 nm;
- (b) introducing a linking moiety onto at least one end of said tubular carbon molecules;
- 5 (c) providing a substrate coated with a material to which said linking moiety will attach; and
- (d) contacting said tubular carbon molecules containing a linking moiety with said substrate.

32. The method of claim 31 wherein said substrate is selected from the
10 group consisting of gold, mercury and indium-tin-oxide.

33. The method of claim 32 wherein said linking moiety is selected from the group consisting of -S-, $-S-(CH_2)_n-NH-$, and $-SiO_3(CH_2)_3NH_2$.

34. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of:

- 15 (a) providing a nanoscale array of microwells on a substrate;
- (b) depositing a metal catalyst in each of said microwells; and
- (c) directing a stream of hydrocarbon or CO feedstock gas at said substrate under conditions that effect growth of single-wall carbon nanotubes from each microwell.

20 35. The method of claim 34 further comprising the step of applying an electric field in the vicinity of said substrate to assist in the alignment of said nanotubes growing from said microwells.

36. A method for forming a macroscopic molecular array of tubular carbon molecules, said method comprising the steps of:

- 25 (a) providing surface containing purified but entangled and relatively endless single-wall carbon nanotube material;
- (b) subjecting said surface to oxidizing conditions sufficient to cause short lengths of broken nanotubes to protrude up from said surface; and

- (c) applying an electric field to said surface to cause said nanotubes protruding from said surface to align in an orientation generally perpendicular to said surface and coalesce into an array by van der Waals interaction forces.

5 37. The method of claim 36 wherein said oxidizing conditions comprise heating said surface to about 500°C in an atmosphere of oxygen and CO₂.

 38. A method of forming a macroscopic molecular array of tubular carbon molecules, said method comprising the step of assembling subarrays of up to 10⁶ single-wall carbon nanotubes into a composite array.

10 39. The method of claim 38 wherein all the subarrays have the same type of nanotubes.

 40. The method of claim 38 wherein the subarrays have different types of nanotubes.

 41. The method of claim 38 wherein the subarrays are made according
15 to the method of any of claims 31, 34 or 36.

 42. A method for continuously growing macroscopic carbon fiber comprising at least about 10⁶ single-wall nanotubes in generally parallel orientation, said method comprising the steps of:

- 20 (a) providing a macroscopic molecular array of at least about 10⁶ tubular carbon molecules in generally parallel orientation and having substantially similar lengths in the range of from about 50 to about 500 nanometers;
- (b) removing the hemispheric fullerene cap from the upper ends of the tubular carbon molecules in said array;
- 25 (c) contacting said upper ends of the tubular carbon molecules in said array with at least one catalytic metal;
- (d) supplying a gaseous source of carbon to the end of said array while applying localized energy to the end of said array to heat said end to a temperature in the range of about 500° C to about 1300° C; and
- 30 (e) continuously recovering the growing carbon fiber.

43. The method of claim 42 wherein said fullerene caps are removed by heating in an oxidative environment.

44. The method of claim 43 wherein said oxidative environment comprises aqueous etching with nitric acid or gas phase etching at temperatures of
5 about 500°C in an atmosphere of oxygen and CO₂.

45. The method of claim 42 wherein said catalytic metal is selected from the group consisting of Group VIII transition metals, Group VI transition metals, metals of the lanthanide series, metals of the actinide series, and mixtures thereof.

46. The method of claim 45 wherein said catalytic metal is selected from
10 the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt.

47. The method of claim 46 wherein said catalytic metal is selected from the group consisting of Fe, Ni, and Co, and mixtures thereof.

48. The method of claim 45 wherein said catalytic metal is selected from the group consisting of Cr, Mo, and W.

49. The method of claim 42 wherein said catalytic metal is deposited in
15 situ on each nanotube as a metal atom cluster.

50. The method of claim 49 wherein said metal atom cluster has from about 10 to about 200 metal atoms.

51. The method of claim 42 wherein said catalytic metal is deposited as
20 preformed nanoparticles.

52. The method of claim 51 wherein said catalytic metal is Mo.

53. The method of claim 42 wherein said catalytic metal is deposited in the form of a metal precursor selected from the group consisting of salts, oxides and complexes of said metal.

54. The method of claim 42 wherein said catalytic metal is deposited by
25 evaporating metal atoms and allowing them to condense and coalesce on said open nanotube ends.

55. The method of claim 54 wherein said evaporation is effected by heating a wire or wires containing said catalytic metal.

56. The method of claim 54 wherein said evaporation is effected by molecular beam evaporation.

57. The method of claim 42 wherein gaseous source of carbon is selected from the group consisting of hydrocarbons and carbon monoxide.

5 58. The method of claim 57 wherein said hydrocarbon is selected from the group consisting of alkyls, acyls, aryls and aralkyl having 1 to 7 carbon atoms.

59. The method of claim 58 wherein said hydrocarbon is methane, ethane, ethylene, acetylene, acetone, propane, propylene and mixtures thereof.

10 60. The method of claim 42 wherein said localized energy is provided by a laser beam.

61. The method of claim 42 wherein said localized energy is provided by a source selected from the group consisting of a microwave generator, an R-F coil and a solar concentrator.

15 62. The method of claim 42 wherein said end is heated to a temperature in the range of about 900°C to about 1100°C.

63. A composition of matter comprising at least about 80% by weight of single-wall carbon nanotubes.

64. The composition of claim 63 comprising at least about 90% by weight of single-wall carbon nanotubes.

20 65. The composition of claim 63 comprising at least about 95% by weight of single-wall carbon nanotubes.

66. The composition of claim 63 comprising at least about 99% by weight of single-wall carbon molecules.

25 67. A substantially two-dimensional article comprising at least about 80% by weight of single-wall carbon nanotubes.

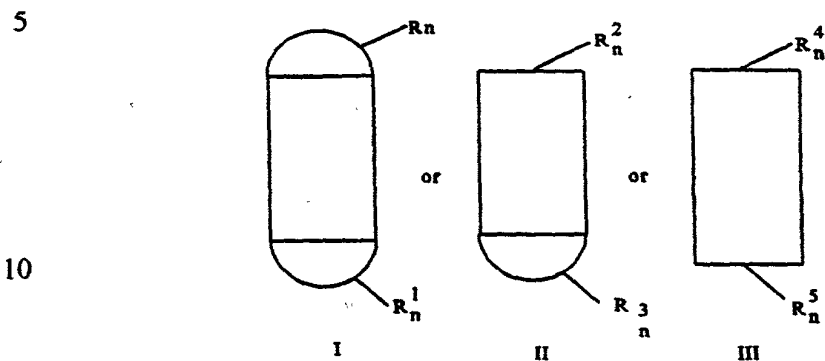
68. The article of claim 67 comprising at least about 90% by weight of single-wall nanotubes.

69. The article of claim 67 comprising at least about 95% by weight of single-wall nanotubes.

70. The article of claim 67 comprising at least about 99% by weight of single-wall nanotubes.

71. The article of claim 67 in the form of a paper-like material.

72. A tubular carbon molecule having the following structure:



where

15



is a substantially defect-free cylindrical graphene sheet (optionally doped with noncarbon atoms) having from about 10^2 to 10^6 carbon atoms;

20

where



is a hemispheric fullerene cap having at least six pentagons and the remainder hexagons;

25

n

is a number from 0 to 30; and

$R, R^1, R^2, R^3, R^4,$ and R^5

each may be independently selected from the group consisting of hydrogen; alkyl, acyl, aryl, aralkyl, halogen; substituted or

30

90

unsubstituted thiol; unsubstituted or substituted amino; hydroxy, and OR' wherein R' is selected from the group consisting of hydrogen, alkyl, acyl, aryl, aralkyl, unsubstituted or substituted amino; substituted or unsubstituted thiol; and halogen; and a linear or cyclic carbon chain optionally interrupted with one or more heteroatom, and optionally substituted with one or more =O, or =S, hydroxy, an aminoalkyl group, an amino acid, or a peptide of 2-8 amino acids.

73. The molecule of claim 72 wherein said graphene sheet has a configuration that corresponds to a (n,n) single-wall carbon nanotube.

74. The molecule of claim 72 wherein said molecule has a length from about 5 to about 1000 nm.

75. The molecule of claim 74 wherein said molecule has a length of from about 5 to about 500 nm.

76. The molecule of claim 72 wherein n is 0 to 12.

77. The molecule of claim 72 further comprising at least one endohedral species.

78. The molecule of claim 77 wherein said endohedral species is selected from the group consisting of metal atoms, fullerene molecules, other small molecules and mixture thereof.

79. The molecule of claim 78 comprising a (10,10) single-wall nanotube containing at least one endohedral species selected from the group consisting of C₆₀, C₇₀, or mixtures thereof.

80. The molecule of claim 79 wherein said C₆₀ or C₇₀ additionally contains an endohedral substituent selected from the group consisting of metal atoms and metal compounds.

81. A macroscopic molecular array comprising at least about 10^6 single-wall carbon nanotubes in generally parallel orientation and having substantially similar lengths in the range of from about 5 to about 500 nanometers.

82. The array of claim 81 wherein said nanotubes are of the same type.

5 83. The array of claim 82 wherein said nanotubes are of the (n,n) type.

84. The array of claim 83 wherein said nanotubes are of the (10,10) type.

85. The array of claim 83 wherein said nanotubes are of the (m,n) type.

86. The array of claim 81 wherein said nanotubes are of different types.

10 87. The array of claim 81 further comprising a substrate attached to one end of said array and oriented substantially perpendicularly to the nanotubes in said array.

88. The array of claim 87 wherein said substrate is a bucky paper surface.

15 89. The array of claim 87 wherein said substrate is a metal layer selected from the group consisting of gold, mercury and indium-tin-oxide.

90. The array of claim 86 wherein a central portion of nanotubes are of the (n,n) type and an outer portion of nanotubes are of the (m,n) type.

20 91. A macroscopic carbon fiber comprising at least about 10^6 single-wall carbon nanotubes in generally parallel orientation.

92. The fiber of claim 91 comprising at least about 10^9 single-wall carbon nanotubes.

93. A composite fiber comprising a plurality of the fibers of claim 91.

25 94. A molecular template array for growing continuous length carbon fiber comprising a segment of the fiber of claim 91.

95. The fiber of claim 91 having a length of at least 1 millimeter.

96. The fiber of claim 91 wherein a substantial portion of said nanotubes are of the (n,n) type.

30 97. The fiber of claim 91 wherein all of said nanotubes are not of the same type.

98. A composite article of manufacture comprising a matrix material selected from the group consisting of metals, polymers, ceramics and cermets, said matrix having embedded in at least a portion thereof a property enhancing amount of the carbon fibers of claim 91.

5 99. The composite article of claim 98 wherein said property is structural, mechanical electrical, chemical, optical, or biological.

100. A high voltage power transmission cable wherein at least one conductor comprises a continuous carbon fiber according to claim 96.

101. The power transmission cable of claim 100 wherein both a central
10 conductor and a coaxially disposed outer conductor are formed from said carbon fiber and an insulating layer is disposed therebetween.

102. The power transmission cable of claim 101 wherein said insulating layer is an air space.

103. The power transmission cable of claim 101 wherein said insulating
15 layer comprises a material selected from the group consisting of insulating carbon fiber made from carbon nanotubes of the (m,n) type and insulating BN fiber made from hexaboronitride nanotubes or mixtures thereof.

104. A solar cell for converting broad spectrum light energy into electrical current comprising a molecular array according to claim 81 as the photon collector.

20 105. The solar cell of claim 104 additionally comprising a photoactive dye coupled to the upper ends of the nanotubes in said array.

106. A bistable, nonvolatile memory bit comprising the endohedrally-loaded tubular carbon molecule of claim 77.

107. The memory bit of claim 106 wherein the tubular carbon molecule
25 is formed from a (10,10) type nanotube and the endohedral species is a C_{60} or C_{70} fullerene molecule.

108. A bistable, nonvolatile memory device comprising the memory bit of claim 106, means for writing to said bit and means for reading said bit.

109. The memory device of claim 108 wherein said means for writing
30 comprises a nanocircuit element adapted to direct a voltage pulse of positive or

negative polarity at said bit to cause said endohedral species to move from a first end to a second end of said bit.

110. The memory device of claim 108 wherein said means for reading said bit comprises

- 5 (a) a first nanocircuit element adapted to be biased at a first voltage (V_{Read}) and spaced from a read end of said bit to form a first gap therebetween; and
- (b) a second nanocircuit element adapted to be biased to ground voltage (V_G) and spaced from said read end of said bit to form a second gap, whereby the presence of said endohedral species is unambiguously determined by the presence
- 10 of current tunneling across said first and second gaps.

111. A microporous anode for an electrochemical cell comprising a molecular array according to claim 81.

112. A lithium ion secondary battery comprising the anode of claim 111, a cathode comprising LiCoO_2 , and an aprotic organic electrolyte wherein a fullerene

15 intercalating compound (FIC) of lithium forms at the anode under charging conditions.

113. An apparatus for forming a continuous macroscopic carbon fiber from a macroscopic molecular template array comprising at least about 10^6 single-wall carbon nanotubes having a catalytic metal deposited on the open ends of said

20 nanotubes, said apparatus comprising:

- (a) means for locally heating only said open ends of said nanotubes in said template array in a growth and annealing zone to a temperature in the range of about 500°C to about 1300°C ;
- (b) means for supplying a carbon-containing feedstock gas to the
- 25 growth and annealing zone immediately adjacent said heated open ends of said nanotubes in said template array; and
- (c) means for continuously removing growing carbon fiber from said growth and annealing zone while maintaining the growing open end of said fiber in said growth and annealing zone.

114. The apparatus of claim 113 wherein said means for locally heating comprises a laser.

115. The apparatus of claim 113 enclosed in a growth chamber maintained at a vacuum by evacuation means.

5 116. The apparatus of claim 115 further comprising a vacuum feed lock zone through which said continuously produced carbon fiber is passed and a take-up roll at atmospheric pressure.

117. A composite material comprising:

- 10 (a) a matrix; and
(b) a carbon nanotube material embedded within said matrix.

118. The composite material of claim 117, wherein said matrix comprises a polymer.

119. The composite material of claim 118, wherein said polymer comprises a thermosetting polymer.

15 120. The composite material of claim 119, wherein said thermosetting polymer is selected from the group consisting of phthalic/maelic type polyesters, vinyl esters, epoxies, phenolics, cyanates, bismaleimides, and nadic end-capped polyimides.

20 121. The composite material of claim 118, wherein said polymer comprises a thermoplastic polymer.

122. The composite material of claim 121, wherein said thermoplastic polymer is selected from the group consisting of polysulfones, polyamides, polycarbonates, polyphenylene oxides, polysulfides, polyether ether ketone, polyether sulfones, polyamide-imides, polyetherimides, polyimides, polyarylates, 25 and liquid crystalline polyesters.

123. The composite material of claim 117, wherein said matrix comprises a metal.

124. The composite material of claim 117, wherein said matrix comprises a ceramic.

125. The composite material of claim 117, wherein said matrix comprises a cermet.

126. The composite material of claim 117, wherein said carbon nanotube material comprises tubular carbon nanotube molecules.

5 127. The composite material of claim 117, wherein said carbon nanotube material comprises ropes up to about 10^3 SWNTs.

128. The composite material of claim 117, wherein said carbon nanotube material comprises fibers of greater than 10^6 SWNTs.

10 129. The composite material of claim 126, 127, or 128, further comprising an additional fibrous material.

130. The composite material of claim 126, 127, or 128, wherein said carbon nanotube material is modified to interact with said matrix material.

131. A method for producing a composite material containing carbon nanotube material comprising:

- 15 (a) preparing a matrix material precursor;
(b) combining a carbon nanotube material with said matrix material precursor; and
(c) forming said composite material.

20 132. The method of claim 131, wherein said carbon nanotube material is combined with said matrix material precursor before said step of forming.

133. The method of claim 131, wherein said carbon nanotube material is combined with said matrix material precursor during said step of forming.

25 134. The method of claim 131, wherein said carbon nanotube material is combined with said matrix material precursor immediately after said step of forming.

135. The method of claim 131, wherein said matrix material precursor is caused to flow around a pre-formed arrangement of said carbon nanotube material.

136. A method of producing a composite material containing carbon nanotube material comprising:

- 30 (a) preparing an assembly of a fibrous material;

- (b) adding said carbon nanotube material to said fibrous material; and
- (c) adding a matrix material precursor to said carbon nanotube material and said fibrous material.

137. The method of claim 136, wherein said fibrous materials are
5 arranged in a two-dimensional sheet, and some portion of the said carbon nanotube material is oriented in a direction other than parallel to said sheet.

138. The method of claim 131 or 136 wherein said carbon nanotube material comprises tubular carbon nanotube molecules.

139. The method of claim 131 or 136, wherein said carbon nanotube
10 material comprises ropes of up to about 10^3 SWNTs.

140. The method of claim 131 or 136, wherein said carbon nanotube material comprises fibers of greater than 10^6 SWNTs.

141. A three-dimensional structure that self-assembles from derivatized single-wall carbon nanotube molecules comprising:

15 a plurality of multifunctional single-wall carbon nanotubes assembled into said three-dimensional structure.

142. The three-dimensional structure of claim 141, wherein said single-wall carbon nanotubes have multifunctional derivatives on their end caps.

143. The three-dimensional structure of claim 141, wherein said single-
20 wall carbon nanotubes have multifunctional derivatives at multiple locations on said single-wall carbon nanotubes.

144. The three-dimensional structure of claim 141, wherein said single-wall carbon nanotubes are assembled as a result of van der Waals attractions.

145. A three-dimensional structure of claim 141, which has
25 electromagnetic properties.

146. The three-dimensional structure of claim 145, wherein said electromagnetic properties are determined by a functionally-specific agent.

147. A three-dimensional structure of claim 141, which is symmetrical.

148. A three-dimensional structure of claim 141, which is not
30 symmetrical.

149. A three-dimensional structure of claim 141, which has biological properties.

150. A three-dimensional structure of claim 149, which operates as a catalyst for biochemical reactions.

5 151. A three-dimensional structure of claim 149, which interacts with living tissue

152. A three-dimensional structure of claim 149, which serves as an agent for interaction with functions of a biological system.

153. A light harvesting antenna comprising:

10 at least one single-wall carbon nanotube conductive element, said at least one nanotube having a length selected relative to a desired current level and a desired voltage level.

154. The light harvesting antenna of claim 153, wherein said at least one single-wall carbon nanotube forms a Schottky barrier.

15 155. An array of light harvesting antennas of claim 153.

156. The array of light harvesting antennas of claim 155, wherein said array is formed by self-assembly.

157. A molecular electronic component comprising at least one single-wall carbon nanotube.

20 158. The molecular electronic component of claim 157, wherein said molecular electronic component is a bridge circuit for providing full wave rectification, said bridge circuit comprising:

four single-wall carbon nanotubes, each of said four single-wall carbon nanotubes forming one edge of a square and linked to two of four
25 buckyballs, each of said four buckyballs located at a corner of said square.

159. The bridge circuit of claim 158, wherein said buckyballs and single-wall carbon nanotubes are derivitized to include functionally specific linking agents.

160. A molecular electronic component of claim 157, which is a fullerene diode.

161. A nanoscale manipulator comprising at least one single-wall carbon nanotube.
162. The nanoscale manipulator of claim 161, which is nanoforceps

1871
 1872
 1873
 1874
 1875
 1876
 1877
 1878
 1879
 1880
 1881
 1882
 1883
 1884
 1885
 1886
 1887
 1888
 1889
 1890
 1891
 1892
 1893
 1894
 1895
 1896
 1897
 1898
 1899
 1900
 1901
 1902
 1903
 1904
 1905
 1906
 1907
 1908
 1909
 1910
 1911
 1912
 1913
 1914
 1915
 1916
 1917
 1918
 1919
 1920
 1921
 1922
 1923
 1924
 1925
 1926
 1927
 1928
 1929
 1930
 1931
 1932
 1933
 1934
 1935
 1936
 1937
 1938
 1939
 1940
 1941
 1942
 1943
 1944
 1945
 1946
 1947
 1948
 1949
 1950
 1951
 1952
 1953
 1954
 1955
 1956
 1957
 1958
 1959
 1960
 1961
 1962
 1963
 1964
 1965
 1966
 1967
 1968
 1969
 1970
 1971
 1972
 1973
 1974
 1975
 1976
 1977
 1978
 1979
 1980
 1981
 1982
 1983
 1984
 1985
 1986
 1987
 1988
 1989
 1990
 1991
 1992
 1993
 1994
 1995
 1996
 1997
 1998
 1999
 2000
 2001
 2002
 2003
 2004
 2005
 2006
 2007
 2008
 2009
 2010
 2011
 2012
 2013
 2014
 2015
 2016
 2017
 2018
 2019
 2020
 2021
 2022
 2023
 2024
 2025
 2026
 2027
 2028
 2029
 2030
 2031
 2032
 2033
 2034
 2035
 2036
 2037
 2038
 2039
 2040
 2041
 2042
 2043
 2044
 2045
 2046
 2047
 2048
 2049
 2050
 2051
 2052
 2053
 2054
 2055
 2056
 2057
 2058
 2059
 2060
 2061
 2062
 2063
 2064
 2065
 2066
 2067
 2068
 2069
 2070
 2071
 2072
 2073
 2074
 2075
 2076
 2077
 2078
 2079
 2080
 2081
 2082
 2083
 2084
 2085
 2086
 2087
 2088
 2089
 2090
 2091
 2092
 2093
 2094
 2095
 2096
 2097
 2098
 2099
 2100
 2101
 2102
 2103
 2104
 2105
 2106
 2107
 2108
 2109
 2110
 2111
 2112
 2113
 2114
 2115
 2116
 2117
 2118
 2119
 2120
 2121
 2122
 2123
 2124
 2125
 2126
 2127
 2128
 2129
 2130
 2131
 2132
 2133
 2134
 2135
 2136
 2137
 2138
 2139
 2140
 2141
 2142
 2143
 2144
 2145
 2146
 2147
 2148
 2149
 2150
 2151
 2152
 2153
 2154
 2155
 2156
 2157
 2158
 2159
 2160
 2161
 2162
 2163
 2164
 2165
 2166
 2167
 2168
 2169
 2170
 2171
 2172
 2173
 2174
 2175
 2176
 2177
 2178
 2179
 2180
 2181
 2182
 2183
 2184
 2185
 2186
 2187
 2188
 2189
 2190
 2191
 2192
 2193
 2194
 2195
 2196
 2197
 2198
 2199
 2200
 2201
 2202
 2203
 2204
 2205
 2206
 2207
 2208
 2209
 2210
 2211
 2212
 2213
 2214
 2215
 2216
 2217
 2218
 2219
 2220
 2221
 2222
 2223
 2224
 2225
 2226
 2227
 2228
 2229
 2230
 2231
 2232
 2233
 2234
 2235
 2236
 2237
 2238
 2239
 2240
 2241
 2242
 2243
 2244
 2245
 2246
 2247
 2248
 2249
 2250
 2251
 2252
 2253
 2254
 2255
 2256
 2257
 2258
 2259
 2260
 2261
 2262
 2263
 2264
 2265
 2266
 2267
 2268
 2269
 2270
 2271
 2272
 2273
 2274
 2275
 2276
 2277
 2278
 2279
 2280
 2281
 2282
 2283
 2284
 2285
 2286
 2287
 2288
 2289
 2290
 2291
 2292
 2293
 2294
 2295
 2296
 2297
 2298
 2299
 2300
 2301
 2302
 2303
 2304
 2305
 2306
 2307
 2308
 2309
 2310
 2311
 2312
 2313
 2314
 2315
 2316
 2317
 2318
 2319
 2320
 2321
 2322
 2323
 2324
 2325